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3-SUBSTITUTED 1-(2-CHLOROTHIAZOL-5-YL-METHYL)-2-NITROIMINO-1,3-DIAZACYCLOALKANES

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(71) Applicant(s)
BAYER AKTIENGESELLSCHAFT

(72) Inventor(s)
HILMAR WOLF; BENEDIKT BECKER; BERNHARD HOMEYER; WILHELM STENDEL

(74) Attorney or Agent
ARTHUR S CAVE & CO, GPO Box 3876, SYDNEY NSW 2001

(56) Prior Art Documents
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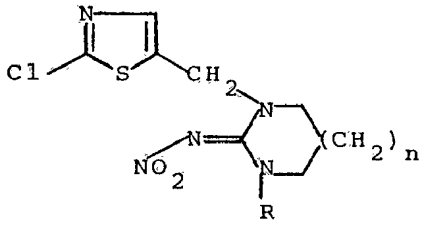
(57) Claim

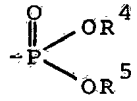
1. 3-Substituted 1-(2-chlorothiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes of the general formula (I)



(I)

in which

n represents 0

R represents C_9-C_{15}-alkyl, C_3-C_6-alkenyl or represents one of the groupings $-CH_2-R^1$, $-CO-R^2$, $-SO_2-R^3$ or  wherein

R^1 represents phenyl substituted by Cl or thiazolyl substituted by Cl,

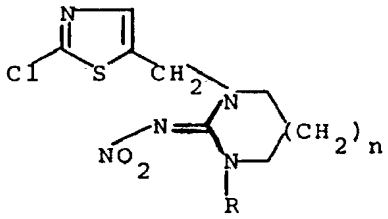
R^2 represents C_1-C_4-alkyl, C_8-C_{18}-alkyl, phenyl substituted by Cl or represents C_5-C_8-alkoxy,

.../2

R^3 represents C_1-C_4-alkyl, and

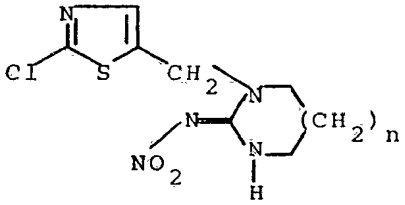
R^4 and R^5 represent C_1-C_3-alkyl.

2. Process for the preparation of 3-substituted 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes of the general formula (I)



(I)

in which n, R, R^1, R^2, R^3, R^4 and R^5 are as defined in claim 1, characterized in that 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacyclo-alkanes of the general formula (II)



(II)

in which

n has the abovementioned meaning,

are reacted with halogen compounds of the general formula (III)

$$X - R \qquad \text{(III)}$$

in which

R has the abovementioned meaning and

X represents halogen,

if appropriate in the presence of an acid acceptor and if appropriate in the presence of a diluent.

3. Agents for combating pests, characterized in that they contain at least one 3-substituted 1-(2-chlorothiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkane of the formula (I), as set forth in claim 1, in admixture with extenders and/or surface active agents.

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COMPLETE SPECIFICATION

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TO BE COMPLETED BY APPLICANT

Name of Applicant:	BAYER AKTIENGESELLSCHAFT
Address of Applicant:	D-5090 Leverkusen, Bayerwerk, Germany
Actual Inventor:	Hilmar Wolf Benedikt Becker Bernhard Homeyer Wilhelm Stendel
Address for Service:	ARTHUR S. CAVE & CO. Patent & Trade Mark Attorneys Level 10 10 Barrack Street SYDNEY N.S.W. 2000 AUSTRALIA

Complete Specification for the invention entitled "3-SUBSTITUTED 1-(2-CHLOROTHIAZOL-5-YL-METHYL)-2-NITROIMINO-1,3-DIAZACYCLOALKANES".
The following statement is a full description of this invention including the best method of performing it known to me:-

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This document contains the amendments made under Section 49 and is correct for printing

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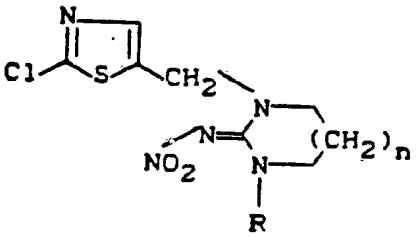
ASC 49

The present invention relates to new 3-substituted 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes, a process for their preparation and their use in agents for combating pests, in particular as insecticides.

It is already known that certain organic nitro compounds, such as, for example, 2-nitromethylene-2H-tetrahydro-1,3-thiazine, have insecticidal properties (compare U.S. Patent Specification 3,993,648).

The new 3-substituted 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes of the general formula (I)



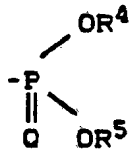
(I)

in which

n represents the numbers 0 or 1 and

R represents methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, C_5-C_{20}-alkyl, C_3-C_{10}-alkenyl or C_3-C_{10}-alkinyl, or represents one of the groupings $-CH_2-R^1$, $-COR^2$, $-S(O)_m-R^3$

or



wherein

R^1 represents in each case an optionally substituted radical from the series comprising phenyl, pyridyl, furyl, thienyl and thiadiazolyl and

R^2 represents methyl - with the proviso that n then represents 0 - or represents optionally sub-

stituted C_2-C_{20}-alkyl, optionally substituted C_3-C_6-cycloalkyl, optionally substituted C_2-C_{20}-alkenyl or optionally substituted phenyl, or represents methoxy, C_3-C_{20}-alkoxy, benzyloxy or phenoxy,

m represents the numbers 0, 1 or 2,

R^3 represents optionally substituted C_1-C_{20}-alkyl, or represents optionally substituted phenyl,

Q represents oxygen or sulphur and

R^4 and R^5 represent C_1-C_4-alkyl,

have now been found.

Preferred possible substituents for R^1 = optionally substituted phenyl are: halogen, cyano, nitro, C_1-C_4-alkyl, trifluoromethyl, C_1-C_4-alkoxy and C_1-C_4-alkoxycarbonyl.

Preferred possible substituents for R^1 = optionally substituted pyridyl are: halogen, cyano, nitro, C_1-C_4-alkyl, trifluoromethyl, C_1-C_4-alkoxy and C_1-C_4-alkoxycarbonyl.

Preferred possible substituents for R^1 = optionally substituted furyl, thienyl, thiazolyl or thiadiazolyl are: halogen, C_1-C_4-alkyl and C_1-C_4-halogenoalkyl.

Preferred possible substituents for R^2 = optionally substituted C_2-C_{20}-alkyl are: halogen, cyano and C_1-C_4-alkoxy.

Preferred possible substituents for R^2 = optionally substituted C_3-C_6-cycloalkyl are: halogen and C_1-C_4-alkyl.

Preferred possible substituents for R^2 = optionally substituted C_2-C_{20}-alkenyl are: halogen.

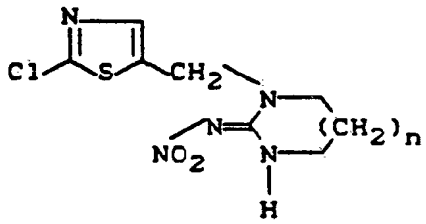
Preferred possible substituents for R^2 = optionally substituted phenyl are: halogen, C_1-C_4-alkyl, trifluoromethyl, cyano, nitro, C_1-C_4-alkoxy and C_1-C_4-alkoxycarbonyl.

Preferred possible substituents for R^3 = option-

ally substituted C_1-C_{20}-alkyl are: halogen.

Preferred possible substituents for R^3 = optionally substituted phenyl are: halogen, C_1-C_4-alkyl, trifluoromethyl, cyano, nitro, C_1-C_4-alkoxy and C_1-C_4-alkoxycarbonyl.

It has furthermore been found that the new 3-substituted 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes of the general formula (I) are obtained by a process in which 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes of the general formula (II)



(II)

in which

n has the abovementioned meaning,

are reacted with halogen compounds of the general formula (III)

$$X - R \qquad \text{(III)}$$

in which

R has the abovementioned meaning and

X represents halogen,

if appropriate in the presence of an acid acceptor and if appropriate in the presence of a diluent.

The new 3-substituted 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes of the formula (I) are distinguished by a high activity as insecticides. Surprisingly, the compounds of the formula (I) according to the invention exhibit a considerably more powerful insecticidal action than organic nitro compounds of comparable structure and action profile, such as, for

example, 2-nitromethylene-2H-tetrahydro-1,3-thiazine.

The invention preferably relates to compounds of the formula (I),

in which

n represents zero and

R represents methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or C_5-C_{18}-alkyl, or represents C_3-C_6-alkenyl or C_3-C_4-alkinyl, or represents the grouping $-CH_2-R^1$,

in which

R^1 represents phenyl [which is optionally substituted by fluorine, chlorine, methyl, methoxy or C_1-C_2-alkoxy-carbonyl], pyridyl [which is optionally substituted by chlorine or methyl] or furyl, thienyl or thiazolyl [which are optionally substituted by chlorine or methyl],

and in which, furthermore,

R represents the grouping $-CO-R^2$,

in which

R^2 represents C_1-C_{18}-alkyl, C_2-C_{18}-alkenyl, phenyl [which is optionally substituted by fluorine, chlorine, bromine, methyl, trifluoromethyl, cyano, nitro or methoxy] or C_3-C_8-alkoxy,

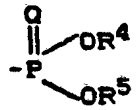
and in which, furthermore,

R represents the grouping $-SO_2-R^3$,

in which

R^3 represents C_1-C_8-alkyl [which is optionally substituted by fluorine or chlorine] or phenyl [which is optionally substituted by fluorine, chlorine, bromine, cyano, nitro, methyl, trifluoromethyl, methoxy, difluoromethoxy, trifluoromethoxy and/or C_1-C_2-alkoxy-carbonyl],

and in which, furthermore,

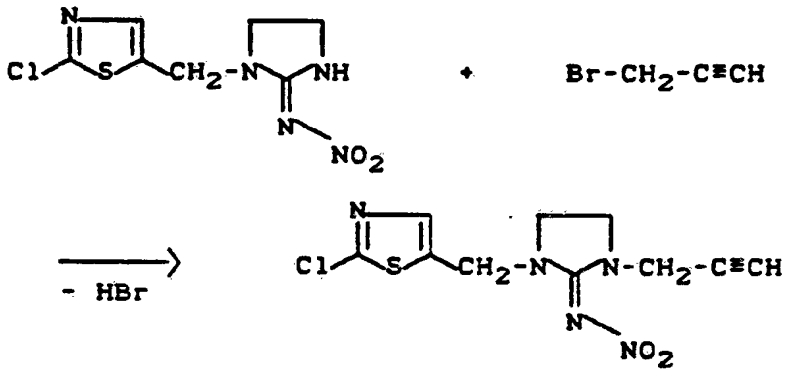
R represents the grouping 

in which

Q represents oxygen or sulphur and

R^4 and R^5 represent C_1-C_3-alkyl.

If, for example, 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-imidazolidine and propargyl bromide are used as starting substances for carrying out the preparation process according to the invention for the compounds of the formula (I), the reaction of these compounds can be outlined by the following equation:



Formula (II) provides a general definition of the 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diaza-cycloalkanes to be used as starting substances in the preparation process according to the invention. In this formula, n preferably represents zero. 1-(2-Chloro-thiazol-5-yl-methyl)-2-nitroimino-imidazolidine is thus preferred as the starting compound of the formula (II).

The starting substances of the formula (II) are already known (compare European Patent A-192,060).

Formula (III) provides a general definition of the halogen compounds furthermore to be used as starting substances. In this formula (III), R preferably represents those radicals which have already been mentioned as preferred for R in connection with the description of the substances of the formula (I) according to the invention, and X preferably represents chlorine or bromine.

Examples which may be mentioned of the starting substances of the formula (III) are:

methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, pentyl, isopentyl, sec-pentyl, hexyl, octyl, decyl, dodecyl, hexadecyl and octadecyl chloride and bromide, allyl, crotyl and propargyl chloride and bromide, benzyl, 4-fluoro-benzyl, 4-chloro-benzyl, 2-chloro-benzyl and 4-methyl-benzyl chloride and bromide, 2-chloro-5-chloro-methyl-pyridine, 2-chloro-5-chloro-methyl-thiazole, acetyl chloride, propionyl and butyryl chloride, pentanoyl, hexanoyl, octanoyl, decanoyl, dodecanoyl, tetradecanoyl, hexadecanoyl and octadecanoyl chloride, acrylyl and crotyl chloride, benzoyl, 4-fluoro-benzoyl, 4-chloro-benzoyl, 4-nitro-benzoyl and 4-methyl-benzoyl chloride, propyl, butyl, pentyl, hexyl, heptyl and octyl chloro-formate, methane-, ethane-, chloro-methane-, trifluoromethane-, tetrafluorobutane- and perfluorooctane-sulphonyl chloride, benzene-, 2-fluoro-benzene-, 2-chloro-benzene-, 4-chloro-benzene-, 2,5-dichloro-benzene-, 2-bromo-benzene, 2-cyano-benzene-, 2-nitro-benzene-, 4-nitro-benzene-, 2-trifluoromethyl-benzene-, 2-methyl-benzene-, 4-methyl-benzene-, 2-methoxy-benzene-, 2-difluoromethoxy-benzene-, 2-trifluoromethoxy-benzene-, 4-trifluoromethoxy-benzene-, 2-methoxycarbonyl-benzene-, 4-methoxycarbonyl-benzene-and 2-ethoxycarbonyl-benzene-sulphonyl chloride, phos-phoric acid chloride-dimethyl ester and -diethyl ester and thiophosphoric acid chloride-dimethyl ester and -diethyl ester.

The starting substances of the formula (III) are known chemical compounds.

The process according to the invention for the preparation of the new compounds of the formula (I) is preferably carried out using diluents. Possible diluents here are virtually all the inert organic solvents. These include, preferably, aliphatic and aromatic, optionally halogenated hydrocarbons, such as pentane, hexane, heptane, cyclohexane, petroleum ether, benzine, ligroin, benzene, toluene, xylene, methylene chloride, ethylene

chloride, chloroform, carbon tetrachloride, chlorobenzene and o-dichlorobenzene, ethers, such as diethyl ether, dibutyl ether, glycol dimethyl ether, diglycol dimethyl ether, tetrahydrofuran and dioxane, ketones, such as acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone, esters, such as methyl and ethyl acetate, nitriles, such as, for example, acetonitrile and propionitrile, amides, such as, for example, dimethylformamide, dimethylacetamide and N-methylpyrrolidone, and dimethylsulphoxide, tetramethylene sulphone and hexamethylphosphoric acid triamide.

Acid acceptors which can be used in the process according to the invention are all the acid-binding agents which can usually be employed for such reactions. Preferred possible acid-binding agents are alkali metal hydrides, such as, for example, sodium hydride, alkali metal hydroxides, such as, for example, sodium hydroxide and potassium hydroxide, alkaline earth metal hydroxides, such as, for example, calcium hydroxide, alkali metal carbonates and alcoholates, such as sodium carbonate, potassium carbonate, sodium methylate or ethylate and potassium methylate or ethylate, and furthermore aliphatic, aromatic or heterocyclic amines, for example triethylamine, trimethylamine, dimethylaniline, dimethylbenzylamine, pyridine, 1,5-diazabicyclo-[4,3,0]-non-5-ene (DBN), 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) and 1,4-diazabicyclo-[2,2,2]-octane (DABCO).

The reaction temperatures can be varied within a substantial range in the process according to the invention. The reaction is in general carried out at temperatures between 0°C and 150°C, preferably at temperatures between 10°C and 100°C.

The process according to the invention is in general carried out under atmospheric pressure.

For carrying out the process according to the invention, the starting substances of the formulae (II)

and (III) are in general employed in approximately equimolar amounts. The starting substances are in general mixed with the acid acceptor and the diluent at room temperature and the reaction mixture is stirred at the stated reaction temperature until the reaction has ended. Working up can be carried out by customary methods.

The active compounds are suitable for combating animal pests, preferably arthropods and nematodes, in particular insects and arachnids, encountered in agriculture, in forestry, in the protection of stored products and of materials, and in the hygiene field. They are active against normally sensitive and resistant species and against all or some stages of development. The abovementioned pests include:

From the order of the Isopoda, for example, Oniscus asellus, Armadillidium vulgare and Porcellio scaber. From the order of the Diplopoda, for example, Blaniulus guttulatus. From the order of the Chilopoda, for example, Geophilus carpophagus and Scutigera spec. From the order of the Symphyla, for example, Scutigerella immaculata. From the order of the Thysanura, for example, Lepisma saccharina. From the order of the Collembola, for example, Onychiurus armatus. From the order of the Orthoptera, for example, Blatta orientalis, Periplaneta americana, Leucophaea maderae, Blattella germanica, Acheta domesticus, Gryllotalpa spp., Locusta migratoria migratorioides, Melanoplus differentialis and Schistocerca gregaria. From the order of the Dermaptera, for example, Forficula auricularia. From the order of the Isoptera, for example, Reticulitermes spp.. From the order of the Anoplura, for example, Phylloxera vastatrix, Pemphigus spp., Pediculus humanus corporis, Haematopinus spp. and Linognathus spp. From the order of the Mallophaga, for example, Trichodectes spp. and Damalinea spp. From the order of the Thysanoptera, for example, Hercinothrips femoralis and Thrips tabaci. From the order of the Heteroptera, for example, Eurygaster spp., Dysdercus

intermedius, Piesma quadrata, Cimex lectularius, Rhodnius prolixus and Triatoma spp. From the order of the Homoptera, for example, Aleurodes brassicae, Bemisia tabaci, Trialeurodes vaporariorum, Aphis gossypii, Brevicoryne brassicae, Cryptomyzus ribis, Aphis fabae, Doralis pomi, Eriosoma lanigerum, Hyalopterus arundinis, Macrosiphum avenae, Myzus spp., Phorodon humuli, Rhopalosiphum padi, Empoasca spp., Euscelis bilobatus, Nephotettix cincticeps, Lecanium corni, Saissetia oleae, Laodelphax striatellus, Nilaparvata lugens, Aonidiella aurantii, Aspidiotus hederae, Pseudococcus spp. and Psylla spp. From the order of the Lepidoptera, for example, Pectinophora gossypiella, Bupalus piniarius, Cheimatobia brumata, Lithocolletis blancardella, Hyponomeuta padella, Plutella maculipennis, Malacosoma neustria, Euproctis chrysorrhoea, Lymantria spp. Bucculatrix thurberiella, Phyllocnistis citrella, Agrotis spp., Euxoa spp., Feltia spp., Earias insulana, Heliothis spp., Spodoptera exigua, Mamestra brassicae, Panolis flammea, Prodenia litura, Spodoptera spp., Trichoplusia ni, Carpocapsa pomonella, Pieris spp., Chilo spp., Pyrausta nubilalis, Ephestia kuehniella, Galleria mellonella, Tineola bisselliella, Tinea pellionella, Hofmannophila pseudospretella, Cacoecia podana, Capua reticulana, Choristoneura fumiferana, Clysia ambiguella, Homona magnanima and Tortrix viridana. From the order of the Coleoptera, for example, Anobium punctatum, Rhizopertha dominica, Acanthoscelides obtectus, Acanthoscelides obtectus, Hylotrupes bajulus, Agelastica alni, Leptinotarsa decemlineata, Phaedon cochleariae, Diabrotica spp., Psylliodes chrysocephala, Epilachna varivestis, Atomaria spp., Oryzaephilus surinamensis, Anthonomus spp., Sitophilus spp., Otiorrhynchus sulcatus, Cosmopolites sordidus, Ceuthorrhynchus assimilis, Hypera postica, Dermestes spp., Trogoderma spp., Anthrenus spp., Attagenus spp., Lyctus spp., Meligethes aeneus, Ptinus spp., Niptus hololeucus, Gibbium psylloides, Tribolium spp., Tenebrio molitor, Agriotes spp., Conoderus spp., Melolontha melolontha, Amphimallon solsti-

tialis and Costelytra zealandica. From the order of the Hymenoptera, for example, Diprion spp., Hoplocampa spp., Lasius spp., Monomorium pharaonis and Vespa spp. From the order of the Diptera, for example, Aedes spp., Anopheles spp., Culex spp., Drosophila melanogaster, Musca spp., Fannia spp., Calliphora erythrocephala, Lucilia spp., Chrysomyia spp., Cuterebra spp., Gastrophilus spp., Hypobosca spp., Stomoxys spp., Oestrus spp., Hypoderma spp., Tabanus spp., Tannia spp., Bibio hortulanus, Oscinella frit, Phorbia spp., Pegomyia hyoscyami, Ceratitis capitata, Dacus oleae and Tipula paludosa. From the order of the Siphonaptera, for example, Xenopsylla cheopis and Ceratophyllus spp. From the order of the Arachnida, for example, Scorpio maurus and Latrodectus mactans. From the order of the Acarina, for example, Acarus siro, Argas spp., Ornithodoros spp., Dermanyssus gallinae, Eriophyes ribis, Phyllocoptruta oleivora, Boophilus spp., Rhipicephalus spp., Amblyomma spp., Hyalomma spp., Ixodes spp., Psoroptes spp., Chorioptes spp., Sarcoptes spp., Tarsonemus spp., Bryobia praetiosa, Panonychus spp., and Tetranychus spp..

The phytoparasitic nematodes include Pratylenchus spp., Radopholus similis, Ditylenchus dipsaci, Tylenchulus semipenetrans, Heterodera spp., Meloidogyne spp., Aphelenchoides spp., Longidorus spp., Xiphinema spp. and Trichodorus spp..

The active compounds of the formula (I) according to the invention are distinguished by an outstanding insecticidal activity. They have an outstanding action, in particular, when used as leaf insecticides and soil insecticides, against for example against rice cicadas (for example Nephotettix cincticeps), against leaf aphids (for example Myzus persicae) and against beetle larvae (for example Phaedon cochleariae).

The active compounds of the formula (I) according to the invention are also suitable for combating arthropods which infest agricultural stock animals, such as,

for example, cattle, sheep, goats, horses, pigs, asses, camels, buffalo, rabbits, chickens, turkeys, ducks, geese and bees, other pets, such as, for example, dogs, cats, canaries and aquarium fish, and so-called experimental animals, such as, for example, hamsters, guineapigs, rats and mice. By combating these arthropods, fatalities and reductions in yield (in meat, milk, wool, hides, eggs, honey and the like) are said to be reduced, so that more profitable and simpler animal husbandry is possible by using the active compounds according to the invention.

In the veterinary sector, the active compounds according to the invention are used in a known manner by enteral administration in the form of, for example, tablets, capsules, drinks, drenches, granules, pastes and boli, of the feed-through process or of suppositories, by parenteral administration, such as, for example, by injections (intramuscular, subcutaneous, intravenous, intraperitoneal and others) or implants, by nasal administration, by dermal use in the form of, for example, dipping or bathing, spraying, pouring on and spotting on, washing or dusting and with the aid of shaped articles containing the active compound, such as neck collars, ear tags, tail tags, limb tapes, halters, marking devices and the like.

Depending on their particular physical and/or chemical properties, the active compounds can be converted to the customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols, natural and synthetic materials impregnated with active compound, very fine capsules in polymeric substances and in coating compositions for seed, and formulations used with burning equipment, such as fumigating cartridges, fumigating cans, fumigating coils and the like, as well as ULV cold mist and warm mist formulations.

These formulations are produced in known manner, for example by mixing the active compounds with extenders,

that is, liquid solvents, liquefied gases under pressure, and/or solid carriers, optionally with the use of surface-active agents, that is emulsifying agents and/or dispersing agents, and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents. As liquid solvents, there are suitable in the main: aromatics, such as xylene, toluene or alkyl naphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethylsulphoxide, as well as water; by liquefied gaseous extenders or carriers are meant liquids which are gaseous at atmospheric temperature and under atmospheric pressure, for example aerosol propellant, such as halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide; as solid carriers there are suitable: for example ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly dispersed silicic acid, alumina and silicates; as solid carriers for granules there are suitable: for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; as emulsifying and/or foam-forming agents there are suitable: for example non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates, aryl sulphonates as well as albumin hydrolysation products; as

dispersing agents there are suitable: for example lignin-sulphite waste liquors and methylcellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, as well as natural phospholipids, such as cephalins and lecithins, and synthetic phospholipids, can be used in the formulations. Other additives can be mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations in general contain between 0.1 and 95 per cent by weight of active compound, preferably between 0.5 and 90%.

The active compounds can be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with other active compounds, such as insecticides, baits, sterilizing agents, acaricides, nematicides, fungicides, growth-regulating substances or herbicides. The insecticides include, for example, phosphates, carbamates, carboxylates, chlorinated hydrocarbons, phenylureas and substances produced by micro-organisms, inter alia.

The active compounds can furthermore be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with synergistic agents. Synergistic agents are compounds which increase the action of the active compounds, without it being necessary for the synergistic agent added to be active itself.

The active compound content of the use forms prepared from the commercially available formulations can

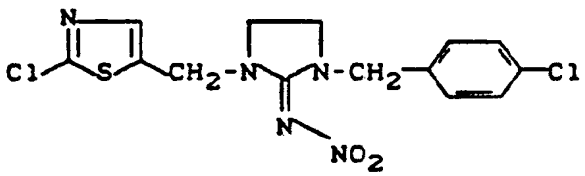
vary within wide limits. The active compound concentration of the use forms can be from 0.0000001 to 95% by weight of active compound, preferably between 0.0001 and 1% by weight.

The compounds are employed in a customary manner appropriate for the use forms.

When used against hygiene pests and pests of stored products, the active compounds are distinguished by an excellent residual action on wood and clay as well as a good stability to alkali on limed substrates.

Preparation Examples

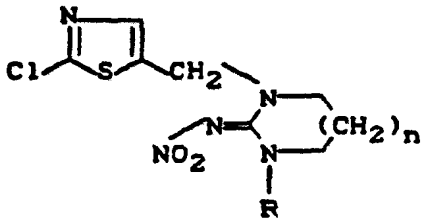
Example 1



A mixture of 3.1 g (0.012 mol) of 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-imidazolidine, 1.9 g (0.012 mol) of 4-chloro-benzyl chloride, 1.6 g (0.012 mol) of potassium carbonate and 50 ml of acetonitrile is heated under reflux for four hours, with stirring. After cooling, the mixture is filtered and the solvent is distilled off from the filtrate under a waterpump vacuum. The residue which remains is stirred with 50 ml of diethyl ether and the product obtained as crystals is isolated by filtration with suction.

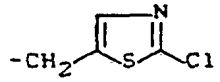
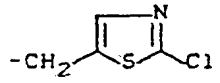
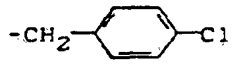
3.65 g (79% of theory) of 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-3-(4-chloro-benzyl)-imidazolidine of melting point 96°C are obtained.

The compounds of the formula (I) listed in the following table can be prepared analogously to Example 1 and in accordance with the general description of the preparation process according to the invention.



(I)

Table: Other examples of compounds of the formula (I)

Example No.	n	-R	Melting point (°C)
2	0		90
3	1		
4	0	$-CH_2-CH=CH_2$	(*)
5	1	$-CH_2-CH=CH_2$	
6	1		
7	0		165
8	1		
9	0	$-SO_2-CH_3$	163
10	1	$-SO_2-CH_3$	
11	0	$-CO-CH_3$	124
12	1	$-CO-CH_3$	
13	0	$-P(OC_2H_5)_2$ (O)	103

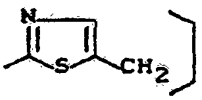
(*) δ_{CH_2}: 4,62 [^{1}H-NMR-Signal for ]

Table - Continuation

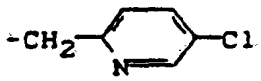
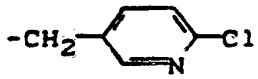
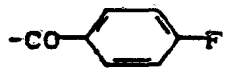
EXAMPLE No.	n	-R	MELTING POINT (°C)
14	1	$-P(OC_2H_5)_2$ (O)	
15	0	$-CO-(CH_2)_{10}-CH_3$	101
16	1	$-CO-(CH_2)_{10}-CH_3$	
17	0	$-(CH_2)_{11}-CH_3$	124
18	1	$-(CH_2)_{11}-CH_3$	
19	0	$-CO-(CH_2)_{16}-CH_3$	102
20	1	$-CO-(CH_2)_{16}-CH_3$	
21	0	$-COO-(CH_2)_7-CH_3$	73
22	1	$-COO-(CH_2)_7-CH_3$	
23	0	$-CH_2-C\equiv CH$	
24	1	$-CH_2-C\equiv CH$	
25	0		
26	0		
27	0	$-CH_2-CH=CH-CH_3$	
28	0		
29	0		

Table - Continuation

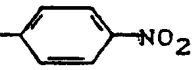
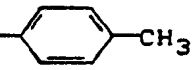
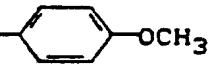
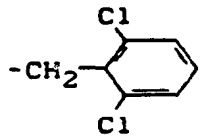
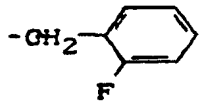
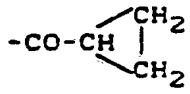
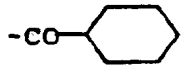
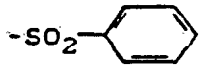
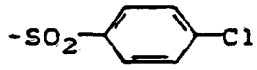
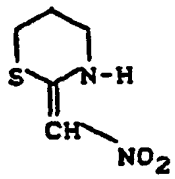
EXAMPLE No.	n	-R	MELTING POINT (°C)
30	0		
31	0		
32	0		
33	0	$-SO_2-C_4H_9$	
34	0	$-SO_2-CH_2Cl$	
35	0	$-SO_2CF_3$	
36	0	$-CO-CH(CH_3)_2$	
37	0	$-CO-C_4H_9$	
38	0	$-P(=S)(OC_2H_5)_2$	
39	0	$-CH_3$	
40	0	$-C_2H_5$	
41	0	$-CH(CH_3)_2$	
42	0	$-CH_2-CH(CH_3)_2$	
43	0	$-C_5H_{11}$	
44	0	$-C_6H_{13}$	
45	0	$-COOC_4H_9$	

Table - Continuation

EXAMPLE No.	n	-R	MELTING POINT (°C)
46	0		
47	0		
48	0		
49	0		
50	0		
51	0		
52	0		

Use Examples

The compound shown below is employed as the comparison substance in the use examples which follow:



(A)

2-Nitromethylene-2H-tetrahydro-1,3-thiazine (compare U.S. Patent Specification 3,993,648).

Example A

Nephottettix test

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent and the stated amount of emulsifier, and the concentrate is diluted with water to the desired concentration.

Rice seedlings (Oryza sativa) treated by being dipped into the preparation of active compound of the desired concentration and are infested with the green rice cicada as long as the seedlings are still moist.

After the specified period of time, the destruction in % is determined. 100% means that all the cicadas have been killed; 0% means that none of the cicadas have been killed.

In this test, for example, the compounds obtained according to Preparation Examples (1), (4), (2), (7), (11), (13), (15) and (21) show an action of 70% - 100% after 6 days at an active compound concentration of 0.0001%, whereas comparison substance (A) shows an action of only 20%.

Example B

Myzus test

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent and the stated amount of emulsifier, and the concentrate is diluted with water to the desired concentration.

Cabbage leaves (Brassica oleracea) which have been heavily infested with the peach aphid (Myzus persicae) are treated by being dipped into the preparation of active compound of the desired concentration.

After the specified periods of time, the destruction in % is determined. 100% means that all the aphids have been killed; 0% means that none of the aphids have been killed.

In this test, for example, the compounds obtained according to Preparation Examples (1), (2), (4), (11) and (13) show an action of 60% - 90% after 1 day at an active compound concentration of 0.001%, whereas comparison substance (A) shows an action of only 10%.

Example C

Critical concentration test / root-systemic action

Test insect: Phaedon cochleariae larvae

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

The preparation of active compound is intimately mixed with soil. The concentration of the active compound in the preparation is of practically no importance, only the amount by weight of active compound per unit volume of soil, which is given in ppm (= mg/l), being decisive. The treated soil is filled into pots and these are planted with cabbage (Brassica oleracea). The active compound can in this way be taken up from the soil by the roots of the plants and be transported into the leaves.

To demonstrate the root-systemic effect, exclusively the leaves are infested with the abovementioned test animals after 7 days. After a further 2 days, the evaluation is made by counting or estimating the dead animals. The root-systemic action of the active compound is deduced from the mortality figures. It is 100% if all test animals have been killed and 0% if just as many test insects are still alive as in the case of the untreated control.

In this test, for example, the compounds obtained according to Preparation Examples (1), (2), (4), (7), (11), (13), (15) and (17) show an action of 100% at an active compound concentration of 20 ppm, whereas comparison substance (A) shows no detectable action.

Example D

Critical concentration test / root-systemic action

Test insect: Myzus persicae

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

The preparation of active compound is intimately mixed with soil. The concentration of the active compound in the preparation is of practically no importance, only the amount by weight of active compound per unit volume of soil, which is given in ppm (= mg/l), being decisive. The treated soil is filled into pots and these are planted with cabbage (Brassica oleracea). The active compound can in this way be taken up from the soil by the roots of the plants and be transported into the leaves.

To demonstrate the root-systemic effect, exclusively the leaves are infested with the abovementioned test animals after 7 days. After a further 2 days, the evaluation is made by counting or estimating the dead animals. The root-systemic action of the active compound is deduced from the mortality figures. It is 100% if all test animals have been killed and 0% if just as many test insects are still alive as in the case of the untreated control.

In this test, for example, the compounds obtained according to Preparation Examples (1), (2), (4), (7), (9), (11), (13), (15), (17) and (19) show an action of 100% at an active compound concentration of 20 ppm, whereas comparison substance (A) shows no detectable action.

Example E

Test with Lucilia cuprina resistant larvae

Emulsifier: 35 parts by weight of ethylene glycol monomethyl ether

35 parts by weight of nonylphenol polyglycol ether

To produce a suitable preparation of active compound, three parts by weight of active compound are mixed with seven parts by weight of the abovementioned solvent mixture and the concentrate thus obtained is diluted with water to the particular desired concentration.

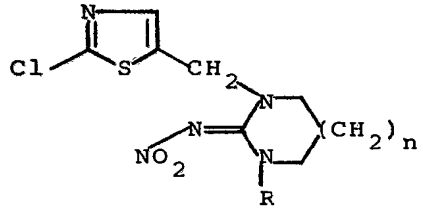
About 20 Lucilia cuprina res. larvae are introduced into a test tube which contains approx. 1 cm^3 of horse muscle and 0.5 ml of the preparation of active compound. After 24 hours, the degree of destruction is determined.

In this test, for example, the flooving compounds from the Preparation Examples show a superior action in comparison with the prior art: (1), (2), (4), (7), (9), (11), (15), (19) and (21).

NOTE: The foregoing description is substantially as originally lodged - and has been retained in this form (i) to preserve the fullness of the initial disclosure, and (ii) for purposes of comparison. The scope of the invention is as defined in the proposed amended claims immediately below.

The claims defining the invention are as follows:

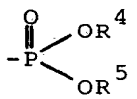
1. 3-Substituted 1-(2-chlorothiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes of the general formula (I)



(I)

in which

n represents O

R represents C_9-C_{15}-alkyl, C_3-C_6-alkenyl or represents one of the groupings $-CH_2-R^1$, $-CO-R^2$, $-SO_2-R^3$ or  wherein

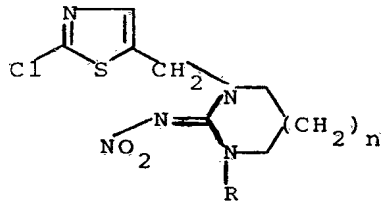
R^1 represents phenyl substituted by Cl or thiazolyl substituted by Cl,

R^2 represents C_1-C_4-alkyl, C_8-C_{18}-alkyl, phenyl substituted by Cl or represents C_5-C_8-alkoxy,

R^3 represents C_1-C_4-alkyl, and

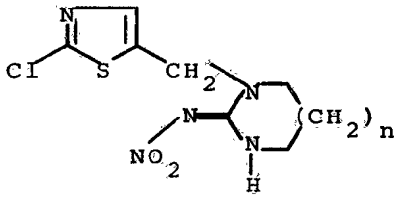
R^4 and R^5 represent C_1-C_3-alkyl.

2. Process for the preparation of 3-substituted 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes of the general formula (I)



(I)

in which n, R, R^1, R^2, R^3, R^4 and R^5 are as defined in claim 1, characterized in that 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacyclo-alkanes of the general formula (II)



(II)

0165c:DW

in which

n has the abovementioned meaning,

are reacted with halogen compounds of the general formula (III)

$$X - R \qquad (III)$$

in which

R has the abovementioned meaning and

X represents halogen,

if appropriate in the presence of an acid acceptor and if appropriate in the presence of a diluent.

3. Agents for combating pests, characterized in that they contain at least one 3-substituted 1-(2-chlorothiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkane of the formula (I), as set forth in claim 1, in admixture with extenders and/or surface active agents.

4. Method of combating animal pests, characterized in that 3-substituted 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes of the formula (I), as set forth in claim 1, are applied to animal pests and/or their environment.

5. Process for the preparation of agents against animal pests, characterized in that 3-substituted 1-(2-chloro-thiazol-5-yl-methyl)-2-nitroimino-1,3-diazacycloalkanes of the formula (I), as set forth in claim 1, are mixed with extenders and/or surface-active agents.

DATED this 23rd day of August, 1990.

BAYER AKTIENGESELLSCHAFT
By Its Patent Attorneys
ARTHUR S. CAVE & CO.

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